



Review of recent developments in Ni-based catalysts for biomass gasification

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ABSTRACT

Biomass gasification is recognized as one of the most promising solutions for renewable energy and environmental sustainability. However, tar formation in gasifier remains as one of the main hurdles that hinder commercialization. Nickel based catalyst is widely used in chemical industries and is proven as one of the most effective transition metal catalysts in biomass gasification for tar cracking and reforming. This paper presents a review of various commercial nickel catalysts that have been evaluated for tar elimination in biomass gasification. This review also looks at recent advancements in nickel based catalyst used in biomass gasification, including discussion on the effects of different support, promoter and particle size on the catalytic performance. Future direction of biomass gasification, including reactive flash volatilization and steam gasification, are also discussed in this review.

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1. Introduction

According to the 2011 Energy White Paper by the Australian Department of Resource, Energy and Tourism, the world global energy demand in year 2035 will be 40% higher than current level [1]. However, with the growing concerns about climate change

and greenhouse gas emissions, non-renewable fossil fuels such as coal, petroleum and natural gas can no longer be considered as the only energy sources for the meeting of our future energy needs. In the short to medium term, a versatile and diverse energy plan, comprising both renewable and non-renewable energy sources is required. In the long term, there is a need for global transition to 100% renewable energy and chemical feedstock to achieve sustainable growth.

Biomass is a renewable energy resource derived from biological sources such as energy crops, agricultural residues, forestry

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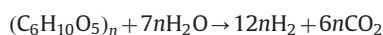
residues and municipal wastes [2]. Biomass utilization is recognized as one of the most promising solutions for our current energy and environmental problems. Alternative renewable energy technologies such as solar energy and wind power, which often suffer from intermittent power generation issue, are less reliable in term of security of supply [3]. Also, biomass is the only renewable energy source that can be converted into liquid fuel and utilized as feedstock in chemicals production [4].

Thermochemical processes for biomass conversion, such as combustion, gasification and pyrolysis, can be used for power generation and biofuels production [5]. Among these processes, biomass gasification has attracted the most attention from both industrial and academic researchers due to its high conversion efficiency [6]. Biomass gasification is a process to convert biomass feedstock into combustible gaseous products like hydrogen, carbon monoxide and methane; however, undesirable products like tar and char are also produced under high temperature and limited oxygen supply environment.

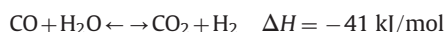
Chemistry of biomass gasification is complex and yet to be fully understood by researchers [7]. It is generally acceptable to say that the major reactions include pyrolysis, oxidation, partial oxidation, reduction, steam reforming and water–gas shift reactions [4,8,9]. Pyrolysis is an endothermic decomposition process which takes place at high temperature in the absence of air or steam. In biomass pyrolysis, the feedstock is converted into gas, liquid tar and solid char products [10] as shown in Fig. 1.

In oxidation or partial oxidation reactions, carbonaceous products from pyrolysis reaction may react further with oxygen to generate more gas and release heat. In the final step of gasification, product gases are upgraded through steam reforming, which converts low molecular weight hydrocarbons such as CH₄ into CO and H₂. Water–gas shift reaction further converts CO and steam into H₂ and CO₂. Side reactions such as methanation also occur in gasification but to a lesser extent [11,12]. Using cellulose as a model, the main chemical reactions of biomass gasification can be expressed in the equations below

overall cellulose steam reforming



water–gas shift



methanation



methane steam reforming



Biomass gasification produces condensable heavy hydrocarbons, generally referred to as tar. Tar removal is a major hurdle that hinders the commercialization of the biomass gasification [4]. Accumulation of tar in the gasifier may lead to severe operational problems such as corrosion, clogging and low gasification

efficiency. Recently, significant progress has been made in the gasifier designs coupled with the use of catalysts to overcome these operational problems. The key focus of this paper is to review some of the recent developments in nickel based catalyst used in biomass gasification and tar removal.

2. Tar

Tar consists of more than 100 different compounds and is produced in a series of complex thermochemical reactions. The amount of tar produced in biomass gasification is greatly affected by factors such as type of biomass feedstock, particle size, type of gasifier, type of gasifying agent and operating conditions such as temperature and pressure. Table 1 shows an overview of different types of biomass gasification setups. Majority of the gasifiers are operated in a temperature range of 700–1000 °C. Generally, higher operating temperatures lead to lower tar content in the product gas. Among the three designs listed in Table 1, gas product generated from entrained flow gasifier normally has the lowest tar content because they operate at the higher end of the gasification temperature range (1000–1400 °C) [13]. Increasing the pressure of gasifiers also has a positive effect in reducing or eliminating the tar formation [14]. However, it has been observed that increasing the pressure results in greater reduction of light hydrocarbons compared to the heavy hydrocarbons, therefore the fraction of polynuclear aromatic hydrocarbons (PAH) in the tar increases with pressure [15].

In addition to the quantity of tar produced, the composition of tar also depends on the type of biomass feedstock, particle size and gasification conditions used. Fraga et al. [16] showed that the distribution of the furan derivatives in sugarcane bagasse tar was different from the distribution found in silver birch wood tar under the same pyrolysis conditions. Ku et al. demonstrated that the content of PAH found in bamboo pyrolysis tar was higher than the PAH content found in oak and pine wood tar [17]. Furthermore, Qin et al. reported that PAH concentration in tar from sawdust gasification decreased as the gasification temperature increased from 700 °C to 900 °C [18]. Therefore, it is important to understand the composition of tar and the conditions under which different types of tar compounds are formed.

Definition of tar varies widely by study, but it is generally accepted as aromatic hydrocarbons with molecular weight higher than benzene [38]. In order to better understand the characteristics of tar, various ways to classify tar have been suggested. The first approach proposed by Milne et al. [39] divides tar into four groups: primary, secondary, alkyl tertiary and condensed tertiary, based on their experimental results obtained from gas phase thermal cracking reactions. Primary tar, which is defined as low molecular weight oxygenated hydrocarbons, is composed of compounds derived from cellulose, analogous hemicellulose and lignin. Examples of primary tar include levoglucosan and furfurals. Secondary tar is composed of phenolic and olefin compound, including cresol and xylene. Alkyl tertiary tar is composed of methyl derivatives of aromatics such as toluene and the condensed tertiary tar is composed of polynuclear aromatics hydrocarbons (PAH) without the branched molecular groups such as benzene and naphthalene. Alkyl tertiary and condensed tertiary tars are products of condensation reaction of the primary tars at high temperature.

Tar can also be classified based on its components solubility and condensability, as suggested by Kiel et al. [40]. It is crucial to understand the condensability and the solubility of tar compounds because condensation of tar in the reactor may lead to severe operating issues and solubility of tar components may increase the

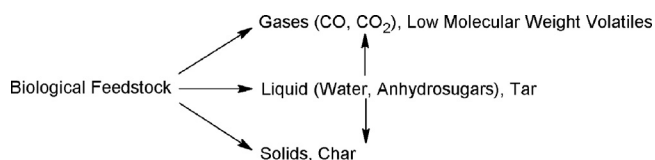


Fig. 1. Pathways for biomass pyrolysis.

Table 1
Comparison of tar content in product gas of different gasification technologies.

Gasifier	Feedstock	Gasifying Agent	Operating conditions		Tar content (g/N m ³ dry gas)	Reference
			Temp (°C)	Pressure (kPa)		
Fixed bed						
Updraft	Straw	Air	400–500	–	~50.0	[19]
Updraft	Sawdust	Air	–	–	8.6	[20]
Updraft	Wood pellet	Air and steam	650	–	90.3	[21]
Updraft	Black pine wood pellet	Air	1000	–	132.4	[22]
Downdraft	Wood chip, municipal solid waste	–	–	–	0.5	[23]
Downdraft	Black pine wood pellet	Air	900	–	32.3	[22]
Downdraft	Hazelnut shell	Air	821–1206	–	2.6–4.0	[24]
Downdraft	Pine wood block	O ₂ and steam	774–934	–	1.7–4.0	[25]
		Air	870–1108	–	7.9–16.7	
		O ₂ and steam	910–1090	–	7.7–21.1	
		Air	798–910	–	1.2–2.5	
Fluidized bed						
Bubbling	Almond shell	Steam	700	–	6.0–7.0	[26]
		Steam	820	–	1.0–1.5	
Bubbling	Pine sawdust	Air	790–810	–	2.0–18.0	[27]
Bubbling	Pine sawdust	Steam	750	~101	180.0	[28]
		Steam	780	~101	40.0	
Bubbling	Pine wood	Steam	750–780	~101	30.0–80.0	[29]
		O ₂ and steam	750–780	~101	4.0–30.0	
		Air	750–780	~101	2.0–20.0	
Bubbling	Wood shaving/saw dust	Air	780	–	~2.0	[30]
		Air	857	–	~0.3	
Bubbling	Rice husk	Air	750	–	6.0	[31]
		Air	940	–	0.8	
Circulating	Mixed sawdust	Air and steam	701	~105	15.1	[32]
			815	~105	0.4	
Pressurized	Pine wood sawdust	Air and steam	700–850	300–1000	5.6	[33]
Entrained flow						
Pressurized	Grapevine pruning, pine sawdust, de-alcoholised marc of grape	Air	750–1050	~101	Negligible	[34]
	Sawdust	Air	700–1000	–	Negligible	[35]
	Coconut coir dust	Air	976	~101	23.6	[36]
			1100	~101	4.8	
	Sawdust from soft stem wood	Oxygen	1000–1200	~195	Negligible	[37]

Table 2
Performance comparison of commercial nickel catalysts used as primary catalyst in biomass gasification and pyrolysis.

Catalyst	NiO (wt%)	Support	BET surface area (m ² /g)	Reactor conditions		Carbon conversion			Reference
				Temp (°C)	Pressure (kPa)	To gas (%)	To solid (%)	To liquid, (%)	
No Catalyst	–	–	–	750	101	80.0	13.0	7.0	Baker et al. [43]
With G-90C	15	70–76% Alumina, 5–8% CaO	3–15	750	101	90.0	10.0	0.0	
No catalyst	–	–	–	728	119	89.8	6.9	3.3	Li et al. [45]
With C11-9 LDP	N/A	Alumina	N/A	739–805	119	95.0–98.3	1.7–4.2	0.0–0.9	

processing cost of the wastewater produced from the process. Based on these two properties, Kiel et al. categorized tar into five classes:

Class 1 – GC undetectable heaviest tars which condense at high temperature and very low concentration.

Class 2 – Heterocyclic aromatic compounds with high water solubility, including phenol and cresol.

Class 3 – Light hydrocarbons aromatic compound (1 ring), a nonissue regarding condensability and solubility, such as toluene and xylene.

Class 4 – Light polyaromatic hydrocarbons (2–3 rings) which condense at relatively high concentrations and intermediate temperatures, including indene and naphthalene.

Class 5 – Heavy polyaromatic hydrocarbons (4–7 rings) which condense at relatively high temperature and low concentration, such as pyrene and coronene.

A comparison of Milne's and Kiel's tar classification approaches is sketched out in Fig. 2. It is clear that definition of tar proposed by Milne et al. covers a broader range of products than definition provided by Kiel et al. All the tar components, from class 1 to class 5, discussed in Kiel et al.'s study fall under secondary and tertiary tar categories according to Milne et al.'s definition. Primary tar compounds lighter than heterocyclic aromatics are not included in Kiel et al.'s classification.

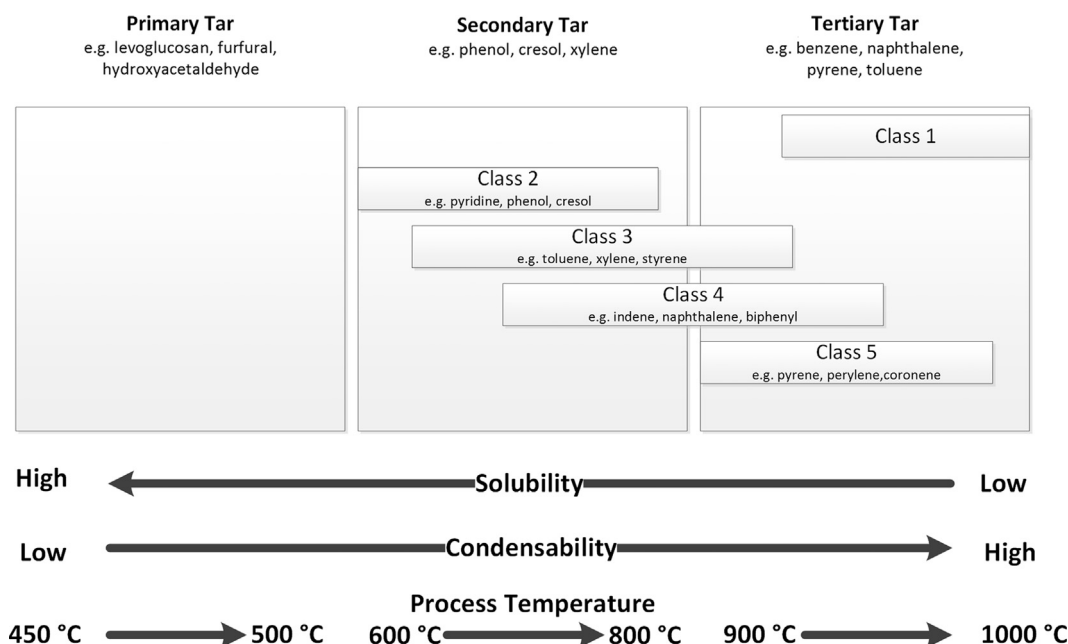


Fig. 2. Comparison of the tar classification methods.

3. Biomass gasification with commercial nickel based catalyst

Significant efforts have been put into developing a cost effective method to eliminate tar in gasification. Among all the proposed solutions, the use of catalysts in gasification *in-situ* is the most promising approach [6,8]. Catalyst used in biomass gasification can be categorized into three types, they are natural mineral catalyst, alkali metal catalyst and transition metal catalyst [8,41]. Dolomite and olivine are two of the most commonly used natural mineral catalysts in biomass gasification. Although the quality of the gaseous product can be improved substantially with these catalysts, additional gas clean-up step is still needed as the quality of the end product is inadequate for direct use in other end user applications, such as fuel cell [42]. Alkali metals, such as lithium, sodium, potassium, and rubidium, have been widely used as catalysts in biomass gasification [41]. Despite the fact that these catalysts provide a considerable increase in initial reaction activity, they are susceptible to loss of activity at high temperature due to particle agglomeration. Alternatively, transition metal-based catalysts, particularly nickel, are excellent for biomass gasification due to their high activities in tar elimination and ability to improve producer gas quality.

A large number of studies have been conducted and reported in the literature using commercial nickel based catalysts in biomass gasification to promote steam-reforming, water–gas shift reactions and to eliminate tar. These studies can be categorized into two groups. The first group focuses on using nickel catalyst as the primary catalyst in the gasifiers and the second group concentrates on using it as the secondary catalyst in post gasification or post pyrolysis reactor.

3.1. Commercial catalyst as primary catalyst

There are several benefits of using nickel catalyst as the primary catalyst. First, nickel is one of the most effective transition metals for tar cracking and reforming [43]. In addition to reducing the tar content, nickel catalyst improves the quality of the gaseous product in biomass gasification. Second, it is economically attractive. Because both gasification and gas clean-up processes occur

in-situ, no downstream reactor or extra heating is required, which results in lower plant capital and operating cost [6,44].

Nonetheless, little work has been reported on using commercial nickel catalyst as primary catalyst in biomass gasification. One study by Baker et al. [43] examined the performance of G-90C catalyst used as primary and secondary catalysts in biomass steam gasification (Table 2). In a fluidized bed experiment with G-90C as primary catalyst, synthesis gas yield of 1.8 m³/kg was obtained in the first 5 h of run. However, gas yield started to decline after 5 h and the catalyst was completely deactivated after 7 h. For comparison, the maximum theoretical gas yield with a H₂/CO ratio of 2.0 is 2.4 m³/kg. Similar behavior was observed in the experiments with G-90C used as a secondary catalyst. The initial activity was high but gradually reduced thereafter. After 16 h of on stream testing, synthesis gas yields of the secondary fixed bed reactor and the secondary fluidized bed reactor stabilized at 1.25–1.30 m³/kg and 1.50 m³/kg respectively. The G-90C catalyst performed better as secondary catalyst over longer time period because of lower carbon fouling (1/3rd) compared to the primary catalyst.

Li et al. [45] also conducted a study using commercial nickel catalyst as primary catalyst in biomass gasification (Table 2). The main focus of their studies was to investigate the impact of operating parameters on the final gaseous product composition in a circulating fluidized bed gasifier and to develop a model for the air-blown circulating fluidized bed biomass gasification. They reported that tar yields in two of the runs with Sud-Chemie catalyst C11-9 LDP were substantially lower when compared with the runs with no catalyst added under the same operating temperature. The tar yield reduced from 10.26 g/N m³ to 2.35 g/N m³ and 0.04 g/N m³ respectively. However, no further investigation and characterization was conducted on the spent catalyst and deactivation of the catalyst was not reported.

Both Baker and Li studies demonstrated the advantages and limitations of commercial nickel catalyst used as primary catalyst in biomass gasification. The catalysts were effective in increasing the gaseous product yield and reducing tar yield. However, the catalysts suffered from rapid deactivation. The deactivation of nickel catalyst in *in-situ* gasification is commonly caused by carbon formation on the catalyst surface and nickel sintering [46]. The deactivation of catalysts in gasification may be minimized

through the use of additives and promoters, which is discussed in Section 4.

3.2. Commercial nickel catalyst as secondary catalyst

Secondary catalysts are used in post gasification or post pyrolysis reactor to improve the quality of the product gas or to reform the bio-oil produced in the primary reactor. Secondary catalysts are active for longer duration because coke formation on the catalyst surface is minimized in a downstream reactor. In this review, studies using nickel catalysts as secondary catalyst will be discussed for upgrading synthesis gas and bio-oil in separate sections. Comparison of the results from literature is listed in Table 3.

3.2.1. Synthesis gas upgrading

Studies conducted by Caballero et al. [47] and Aznar et al. [48] looked into the feasibility of using commercial nickel catalyst as secondary catalyst in biomass gasification. Four out of eight catalysts used in their studies were made for heavy hydrocarbons steam reforming, while the remaining were made for light hydrocarbons steam reforming. Catalysts were tested in a reactor set up shown in Fig. 3 for pine wood chips gasification. It was found that catalysts made for heavy hydrocarbons steam reforming were more effective in eliminating tar, promoting hydrogen and carbon monoxide productions and suppressing the formations of the undesired methane and carbon dioxide [49–51]. No catalyst deactivation was reported after 45 h of on-stream testing in a

temperature range of 780–830 °C. These findings agree with the result reported by Pfeifer et al. [7].

Pfeifer et al. [7] tested six commercial nickel catalysts, also made for heavy and light hydrocarbons reforming, in toluene steam reforming reaction with a fixed bed quartz reactor. They found that heavy hydrocarbons steam reforming catalysts were more effective in converting tars and ammonia into gaseous product than light hydrocarbons reforming catalysts. High conversion of tar (98%) and ammonia (40%) was achieved at a space velocity of 1200 h⁻¹ and operating temperature of 850–900 °C. Selectivity toward CO formation was higher with heavy hydrocarbons reforming catalysts. No deactivation of catalyst was reported from the 12 h test which implies that these catalysts were able to suppress coke deposition.

One of the catalysts, G-90B, studied by Pfeifer was also used by Kinoshita et al. [52] in sawdust gasification investigation. Using in an indirectly heated fluidized bed catalytic reformer, they noticed that carbon conversion, tar conversion and gas yield, particularly carbon monoxide and hydrogen yield, increased as the temperature and space time increased. Complete conversion of tar was achieved at 700–800 °C at space velocity > 1.2 s. Hydrogen to carbon monoxide ratio also improved by increasing steam to biomass ratio. However, increasing the steam to biomass ratio lowers the heating value of the product gas due to high vapor content in the product gas.

In summary, commercial catalysts used in heavy hydrocarbons reforming performed better in converting tar and suppressing coke formation. The nickel loading of the heavy hydrocarbons reforming catalysts is typically 5–10 wt% higher than light hydrocarbons

Table 3
Comparison of the properties of commercially available nickel based catalyst.

Catalyst	NiO content (wt%)	Support	Surface Area (m ² /g)	Reactor temp (°C)	Initial tar conversion (%)	Reference
Heavy hydrocarbons reforming						
BASF						
G1-25/1	25	CaO–Al ₂ O ₃ –SiO ₂ –K ₂ O	16.4	785–850	98–99	[7,50]
G1-50	20	MgO–CaO–Al ₂ O ₃ –SiO ₂ –K ₂ O	19.9	660–800	89–99	[50,51]
Haldor Topsoe						
R-67	15	MgAl ₂ O ₄ –SiO ₂ –K ₂ O	17	780–840	95–100	[50,51]
ICI Katalco						
46-1	22	MgO–CaO–Al ₂ O ₃ –SiO ₂ –K ₂ O	16.2	700–875	73–100	[43,50,51,53,55]
Sud Chemie						
C11-NK	20–25	MgO–CaO–SiO ₂ –Al ₂ O ₃	8.8	600–900	–	[7,53,56]
Light hydrocarbons reforming						
BASF						
G1-25S	12–15		2.5	785	88–97	[47,48]
V1693	10.2		–	850–900	–	[7]
Haldor Topsoe						
RKS-1	15	MgAl ₂ O ₄ –SiO ₂ –K ₂ O	6.8	785–800	92	[47,48,50,51]
R-67-7H	16–18	MgAl ₂ O ₄	12–20	690–780	99	[57]
ICI Katalco						
57-3	12	CaO–Al ₂ O ₃ –SiO ₂	2.9	–	69	[47,48,50,51]
Sud Chemie						
G-90LDP	14	CaO–Al ₂ O ₃	–	850–900	99	[7]
G-90EW	14	CaO–Al ₂ O ₃	–	850–900	99	[7]
G-90B	14	CaO–Al ₂ O ₃	5–7	650–900	99	[7,52]
United Catalyst						
C11-9-061	10–15	Al ₂ O ₃	2.9	725–800	–	[47,48,50,51]

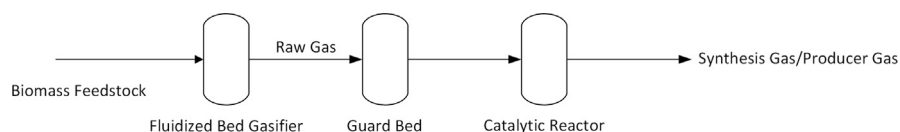


Fig. 3. Simplified reactor setup used in [47,48].

reforming catalysts. The catalyst BET surface area of the heavy hydrocarbons reforming catalyst was on average 3 times the surface area of the light hydrocarbons reforming catalysts. High BET surface area along with higher metal loading would provide large metal surface area which is one of the reasons for better activity of heavy hydrocarbon catalysts. Another reason is the presence of magnesium compounds in the heavy hydrocarbons reforming catalysts. Oxides of magnesium play a key role in suppressing coke formation in gasification [53,54].

3.2.2. Bio-oil steam reforming

Steam reforming of bio-oil with commercial nickel catalyst is a well-studied approach for synthesis gas production [53,55,56]. Bio-oil is produced by fast pyrolysis of biomass and steam reforming of bio-oil produces synthesis gas rich in hydrogen. Composition of bio-oil depends upon biomass type and pyrolysis conditions, however, typical compounds found in bio-oil are saccharides, anhydrosugars, aldehydes, furans, ketones, alcohols, carboxylic acids and aromatics (pyrolytic lignin) [57]. The commercial catalysts are used in the secondary reactor to facilitate bio-oil steam reforming reaction. All the published work reviewed in the paper conclude that the nickel catalysts suffers from rapid deactivation [53,55,56].

Three commercial catalysts were investigated by Wang et al. [55], including G-90C, G-91 from United Catalyst and a dual catalyst 46-1/46-4 from ICI Katalco. By using rapid catalyst screening method, they found that all catalysts were efficient in converting model compounds like methanol, acetic acid, an aqueous solution of hydroxyl-acetaldehyde, a methanol solution of 4-allyl-2,6-dimethoxyphenol and a mixture model compounds of 67% acetic acid, 16% *m*-cresol, and 16% syringol into hydrogen rich gaseous products (> 99%). The dual catalyst 46-1/46-4 was more effective in inhibiting carbonaceous deposition than G-90C and G-91 because the former catalysts contained MgO additive in the support. Further investigation carried out by Garcia et al. [53] demonstrated that similar performance was achieved with commercial catalysts G-91, C11-NK and 46-1/46-4 in steam reforming of poplar wood pyrolysis bio-oil into gaseous product. Carbon conversion into CO and CO₂ started at 85–90% and gradually decreased to 75–85% in 25 min. Decrease in hydrogen and carbon dioxide yields was accompanied by the increase of carbon monoxide, methane, benzene and other aromatics yields during the run which indicated catalyst deactivation.

Deactivation of C11-NK catalyst, used in a bio-oil steam reforming, was also reported by Kechagiopoulos et al. [56]. They reported complete conversion of model compounds including acetone, ethylene, glycol, and acetic acid at temperatures higher than 600 °C, gas hourly space velocity of 1500 h⁻¹ and steam to carbon ratio higher than 3. Hydrogen yield in product gas was as high as 90%. However, steam reforming of aqueous-phase beech wood pyrolysis bio-oil produced lower hydrogen yield at around 60%. The real bio-oil led to substantially higher coke formation compared to the model compounds which led to rapid deactivation and lower hydrogen yield.

The catalysts reviewed in this paper suffered significantly faster deactivation due to coke formation in bio-oil steam reforming compared to synthesis gas upgrading. Hydrogen yield from bio-oil steam reforming using ICI-46 series catalyst and UCI G-91 decreased from 80% to 60% in 300 min and from 75% to 70% in 150 min of run, respectively [55]. Garcia et al. [53] also reported an average drop of 20% in hydrogen yield in 25 min, while the C11-NK catalyst used by Kechagiopoulos et al. [56] deactivated completely after 17 h of run. Coke formation was identified as the primary cause of deactivation. Section 4 reviews the advancements in gasification using nickel catalysts to overcome the coke deposition.

A comparison of catalysts reviewed in this section can also be found in Table 3.

4. Recent advancements in nickel based catalyst for biomass gasification

Various catalyst supports, metal additives and synthesis methods have been developed by researchers to improve stability and activity of nickel catalysts. These studies can be divided into the effect of support material, the effect of promoter and the effect of particle size. Some of the most commonly used support materials include olivine, dolomite [59], alumina [59–61], silica [59–61] and magnesium oxide [60]. Promoter such as platinum [62,63], palladium [62], rhodium [62], ruthenium [62], cobalt [63,64], iron [63] and copper [65] are widely used in catalyst synthesis to improve catalyst performance.

4.1. Effect of support on nickel based catalysts

One of the prominent issues with using nickel catalyst in biomass gasification is rapid loss of catalytic activity due to carbon deposition. Varying degree of success has been achieved in suppressing coke formation by changing the type of support material. Srinakruang et al. [59] studied the effectiveness of three catalyst supports, alumina, silica–alumina mixed oxide and dolomite, in suppressing carbon deposition in gasification. Ni/Al₂O₃ and Ni/SiO₂–Al₂O₃ catalysts were synthesized using impregnation method while Ni/dolomite catalyst was prepared by precipitation–deposition method with aqueous solution of nickel nitrate hexahydrate. Detailed catalyst preparation parameters are listed in Table 4. Catalytic activity of toluene conversion in a fixed bed reactor decreased in the following order Ni/Al₂O₃ > Ni/SiO₂–Al₂O₃ > Ni/dolomite. However, Ni/dolomite catalyst was stable for the longest duration (7 h). Results from thermogravimetric analysis (TGA) showed that the amount of coke formation was in the following order Ni/dolomite < Ni/Al₂O₃ < Ni/SiO₂–Al₂O₃, measured at 0.0 wt%, 1.7 wt% and 7.2 wt% respectively. Srinakruang et al. attributed the better performance of Ni/dolomite catalyst to the basicity of the dolomite support. Basic oxides, such as MgO and CaO found in dolomite, help to promote forming of surface oxide ions which assist in gasifying of deposited carbon.

Kong et al. [60] conducted a study on carbon dioxide reforming of toluene in a fluidized bed reactor with nickel catalyst on various support materials, including alumina, silica, zirconium oxide and magnesium oxide. All the catalysts were prepared by impregnation method. From their studies, they found that Ni/MgO and Ni/α-Al₂O₃ were more stable than other supported catalysts for up to 400 min on stream. Nickel catalyst supported on acidic supports were least coke resistant and the synthesis method play a big role in catalyst stability. Ni/SiO₂ catalyst made by the sol–gel method had the highest surface area (765 m²/g), gas yield (54 wt%) and coke deposition (19.4 wt%) compared to Ni/SiO₂ made by incipient wetness method (136 m²/g, 49.8 wt% and 3.7 wt%, respectively) [61].

Support material plays an important role in defining the activity and service life of the catalyst. Studies reviewed here have concluded that catalyst with high surface area support generally exhibits higher catalytic activity. However, the catalyst support acidity is important for stability. Basic supports such as dolomite and MgO are better at inhibiting carbon fouling [47,48,59,60].

4.2. Promoted nickel based catalyst

Another method to improve the activity and coke resistance of nickel supported catalysts is to dope it with noble metals [62,63],

Table 4
Comparison of nickel catalysts with different support materials used in pyrolysis and steam reforming of bio-oil.

Catalyst	Ni, (wt%)	BET surface area (m ² /g)	Synthesis method	Precursor	Drying temp (°C) (time, h)	Calcination temp (°C) (time, h)	Reduction temp (time, h)	Reaction temp (°C)	Conversion of toluene (%)	Gas yield (wt%)	Coke deposition (wt%)	Reference
Ni/dolomite	15	10.8	PD	Ni(NO ₃) ₂ ·6H ₂ O, dolomite, (NH ₄) ₂ CO ₃	120 (~12)	750 (2)	700 (2) follow by 770 (0.25)	700	92.0 ^a	–	0.0 ^b	[58]
Ni/Al ₂ O ₃	15	322	IWI	Ni(NO ₃) ₂ ·6H ₂ O, Al ₂ O ₃	120 (~12)	750 (2)		700	99.0 ^a	–	1.7 ^b	
Ni/SiO ₂ –Al ₂ O ₃	15	362	IWI	Ni(NO ₃) ₂ ·6H ₂ O, SiO ₂ –Al ₂ O ₃	120 (~12)	750 (2)		700	90.0 ^a	–	7.2 ^b	
Ni/MgO	5	318	IWI	Ni(NO ₃) ₂ , MgO	120 (6)	700 (6)	700 (1)	600	91.0	–	0.3 ^b	[59]
Ni/α-Al ₂ O ₃	5	271	IWI	Ni(NO ₃) ₂ , α-Al ₂ O ₃	120 (6)	700 (6)		600	67.2	–	1.2 ^b	
Ni/γ-Al ₂ O ₃	5	152.7	IWI	Ni(NO ₃) ₂ , γ-Al ₂ O ₃	120 (6)	700 (6)		600	74.2	–	4.1 ^b	
Ni/ZrO ₂	5	8.1	IWI	Ni(NO ₃) ₂ , ZrO ₂	120 (6)	700 (6)		600	32.8	–	3.4 ^b	
Ni/SiO ₂	5	319.4	IWI	Ni(NO ₃) ₂ , SiO ₂	120 (6)	700 (6)		600	11.1	–	3.8 ^b	
Ni/Al ₂ O ₃	20	147	IWI	Ni(NO ₃) ₂ ·6H ₂ O, Al ₂ O ₃	105 (~12)	450 (3)	No reduction	760	–	49.5	–	[60]
Ni/CeO ₂ –Al ₂ O ₃	20	111	IWI	Ni(NO ₃) ₂ ·6H ₂ O, Ce	105 (~12)	450 (3)		760	–	47.6	–	
Ni/SiO ₂	20	136	IWI	Ni(NO ₃) ₂ ·6H ₂ O, SiO ₂	105 (~12)	450 (3)		760	–	49.8	3.7 ^c	
Ni/SiO ₂	20	765	SG	Ni(NO ₃) ₂ ·6H ₂ O, citric acid, ethanol, SiC ₈ H ₂₀ O ₄	80 (~12)	450 (3)		760	–	54.0	19.4 ^c	

PD=precipitation–deposition, IWI=incipient wetness impregnation, SG=sol–gel.

^a Data extracted from the figures.

^b Measured by thermogravimetric analyzer after reaction for 7 h.

^c Measured by X-ray photoelectron spectroscopy after reaction.

alkali metals [65], rare earth metals [62] or transition metals [63–65]. Table 5 compares the experimental parameters and catalyst synthesis methods and Table 6 compares catalysts properties based on chemisorption measurements.

Nishikawa et al. [62] examined the effect of noble metals, including Pt, Pd, Rh and Ru, on the performance of Ni/CeO₂–Al₂O₃ catalyst in cedar wood biomass steam gasification with a laboratory scale continuous feeding dual bed reactor. The Ni/CeO₂–Al₂O₃ was prepared by co-impregnation method, whereas, the noble metal promoter was impregnated later. Although the addition of noble metals, especially Pt, was effective in promoting steam gasification, these additives had minimal effect in inhibiting coke formation. Nonetheless, high catalytic activity of Pt promoted catalyst was the result of the strong interaction between the platinum and nickel metals. They also noted that unreduced platinum catalyst had the same catalytic performance as the reduced catalyst, which suggested that hydrogen pre-treatment may not be required.

Chaiprasert et al. [63] studied Pt, Fe and Co as promoter for Ni catalysts in a fluidized bed coconut shell gasification. Catalysts were prepared by impregnation and co-precipitation methods with 1 wt% promoter and 10 wt% Ni loading on dolomite supported catalysts. XRD analysis suggested that catalysts synthesized by these two methods had similar crystalline structure. Gasification results indicated that the addition of Pt promoter enhanced steam reforming and water–gas shift reactions. Product gas generated had higher concentration of hydrogen, carbon monoxide and carbon dioxide. Fe promoted catalyst was only effective in promoting water–gas shift reaction, which increased the production of hydrogen and carbon dioxide. Cobalt promoted catalyst was more effective in promoting methanation and reforming of methane. While all the three promoters reduced coke deposition, Pt promoted catalyst exhibited the highest coke resistance. Amount of coke deposited onto the Pt, Fe, Co promoted catalysts, and non-promoted catalysts were 6.5, 8.3, 9.3 and 16.5 wt% respectively.

The effect of cobalt concentration on the performance of nickel catalyst in steam reforming of toluene was investigated by Wang et al. [64]. Catalysts were prepared by co-impregnating Co up to 12 wt% onto 12 wt% Ni/Al₂O₃ catalyst. The catalytic activity initially improved with the increase of Co loading up to 3 wt% but later dropped with higher Co loadings. Similar trend was observed in the study of Cu promoted catalytic steam reforming of acetic acid [65]. This behavior can be explained by lowering of nickel surface area at high promoter loading. Nevertheless, Co and Cu promoted nickel catalysts were more effective than non-promoted Ni/Al₂O₃ catalysts in reforming oxygenates and inhibiting coke formation.

In summary, bimetallic catalysts, especially with the noble metal additive such as Pt, performs significantly improves catalytic activity and suppresses coke deposition during gasification.

4.3. Nickel nanoparticle catalyst

A nanoparticle catalyst is defined as a catalyst with a particle size in the range of 1–100 nm [66]. Nanoparticle catalysts can be either unsupported or supported on alumina [67,68], carbon nanotubes [69] and other types of support material. Li et al. [70] conducted several studies supported and unsupported nickel nanoparticle catalyst for biomass pyrolysis. The catalyst used in this study was synthesized using homogenous-precipitation method and had a specific surface area of 187.98 m²/g and cubic crystals size of 7.5 nm. Performance of this nanoparticle catalyst and a commercial nickel based microparticle catalyst was evaluated in a TGA, measured from ambient temperature to 900 °C. The results showed that the cellulose pyrolysis onset temperature with

Table 5
Comparison of promoted nickel catalysts used in pyrolysis and steam reforming of biomass.

Catalyst	Ni (wt%)	Promoter (wt%)	Synthesis method	Precursor	Drying temp (°C) (time, h)	Calcination temp (°C) (time, h)	Reaction temp (°C)	C based gas yield (%)	Coke deposition (wt%) per min of run	Reference
Ni/CeO ₂ -Al ₂ O ₃	4	0	Incipient wetness	Ni(NO ₃) ₂ · 6H ₂ O, Ce(NH ₄) ₂ (NO ₃) ₆ , Al ₂ O ₃	110 (12)	500 (3)	550–650	65–82	0.33	[61]
Pt-Ni/CeO ₂ -Al ₂ O ₃	4	0.1	Incipient wetness	Ni(NO ₃) ₂ · 6H ₂ O, Ce(NH ₄) ₂ (NO ₃) ₆ , Al ₂ O ₃ Pt	110 (12)	500 (3)	550–650	70–82	> 0.33	
Pd-Ni/CeO ₂ -Al ₂ O ₃	4	0.1	Incipient wetness	(NO ₃) ₂ (NH ₃) ₂ Ni(NO ₃) ₂ · 6H ₂ O, Ce(NH ₄) ₂ (NO ₃) ₆ , Al ₂ O ₃ , Pd(NO ₃) ₂	110 (12)	500 (3)	550–650		> 0.33	
Rh-Ni/CeO ₂ -Al ₂ O ₃	4	0.1	Incipient wetness	Ni(NO ₃) ₂ · 6H ₂ O, Ce(NH ₄) ₂ (NO ₃) ₆ , Al ₂ O ₃ , Rh(NO ₃) ₃	110 (12)	500 (3)	550–650	67–83	> 0.33	
Ru-Ni/CeO ₂ -Al ₂ O ₃	4	0.5	Incipient wetness	Ni(NO ₃) ₂ · 6H ₂ O, Ce(NH ₄) ₂ (NO ₃) ₆ , Al ₂ O ₃ , Ru(NO)(NO) ₃	110 (12)	500 (3)	550–650	70–82	> 0.33	
Pt-Ni/dolomite	15	1	Precipitation and impregnation	Ni(NO ₃) ₂ · 6H ₂ O, dolomite, (NH ₄) ₂ CO ₃ , H ₂ PtCl ₆	120 (~12)	600	800	79.19	0.05	[62]
Fe-Ni/dolomite	15	1		Ni(NO ₃) ₂ · 6H ₂ O, dolomite, (NH ₄) ₂ CO ₃ , FeCl ₃	120 (~12)	600	800	78.12	0.07	
Co-Ni/dolomite	15	1		Ni(NO ₃) ₂ · 6H ₂ O, dolomite, (NH ₄) ₂ CO ₃ , Co(NO ₃) ₂	120 (~12)	600	800	49.53	0.08	
Pt-Ni/dolomite	15	1	Co-precipitation	Ni(NO ₃) ₂ · 6H ₂ O, dolomite, (NH ₄) ₂ CO ₃ , H ₂ PtCl ₆	120 (~12)	600	800	50.51		
Fe-Ni/dolomite	15	1		Ni(NO ₃) ₂ · 6H ₂ O, dolomite, (NH ₄) ₂ CO ₃ , FeCl ₃	120 (~12)	600	800	57.46		
Co-Ni/dolomite	15	1		Ni(NO ₃) ₂ · 6H ₂ O, dolomite, (NH ₄) ₂ CO ₃ , Co(NO ₃) ₂	120 (~12)	600	800	41.82		
Co-Ni/Al ₂ O ₃	12	0.72–12	Co-impregnation	Ni(NO ₃) ₂ · 6H ₂ O, Co(NO ₃) ₂ · 6H ₂ O, Al ₂ O ₃	110 (12)	500 (3)	550	54–68	0.01	[63]

Table 6
Comparison of chemisorption results of various research based nickel catalysts.

Catalyst	Ni content (wt%)	Promoter content (wt%)	BET surface area (m ² /g)	Reduction degree (TPR) (%)	Particle size of Ni (nm)	H ₂ adsorption @298 K (10 ⁻⁶ mol/g _{cat})	Dispersion	H ₂ consumption in TPR (10 ⁻³ mol/g _{cat})	Metal surface area (m ² /g)	Reference
Ni/MgO	5	0	31.8	8	Not determined					[59]
Ni/α-Al ₂ O ₃	5	0	27.1	76	9.9					
Ni/γ-Al ₂ O ₃	5	0	152.7	11	7.9					
Ni/ZrO ₂	5	0	8.1	97	20.7					
Ni/SiO ₂	5	0	319.4	101	22.1					
Ni/CeO ₂ -Al ₂ O ₃	4	0	15	149		40	5.8	1.02		[61]
Pt-Ni/CeO ₂ -Al ₂ O ₃	4	0.1	14–15	142		57	8.4	0.97		
Pd-Ni/CeO ₂ -Al ₂ O ₃	4	0.1	18	138		55	8.0	0.95		
Rh-Ni/CeO ₂ -Al ₂ O ₃	4	0.1	16	144		61	9.0	1.0		
Ru-Ni/CeO ₂ -Al ₂ O ₃	4	0.5	15	146		62	9.0	1.1		
Pt-Ni/dolomite	15	1	6.74		77				0.97	[62]
Fe-Ni/dolomite	15	1	5.76		364				0.20	
Co-Ni/dolomite	15	1	11.18		2671				0.03	
Pt-Ni/dolomite	15	1	5.33		166				0.06	
Fe-Ni/dolomite	15	1	4.77		1532				0.05	
Co-Ni/dolomite	15	1	8.76		2715				0.02	
Co-Ni/Al ₂ O ₃	12	0.72–12	N/A		25–34	47–57	2.7–4.7	2.1–4.9		[63]

the nanoparticle catalyst was slightly lower than the onset temperature with the microparticle catalyst, measured at 294 °C and 303 °C respectively. Lower onset temperatures were also observed in hemicellulose and lignin pyrolysis with nanoparticle catalyst, which indicated that the nanoparticle catalyst help to lower the activation energy required for pyrolysis reaction.

Supported nanoparticle catalysts, Ni/Al₂O₃ and Ni–La–Fe/Al₂O₃, were developed by Li et al. [67,68,71] using the deposition–precipitation method and tested for sawdust pyrolysis reaction. Both the catalysts demonstrated excellent tar conversion (> 99%) at a temperature of 800 °C, significantly improving in the quality of the product gas, especially CO, CO₂, CH₄ and C₂ yields. Similar results were reported by Liu et al. [71] and Feng et al. [72] who studied the nano-NiO/γ-Al₂O₃ in municipal solid waste and sawdust steam gasification. Li et al. reported that the nanoparticle Ni/Al₂O₃ and the Ni–La–Fe/Al₂O₃ catalysts negligible to no deactivation, respectively, in the 10 h sawdust pyrolysis life test studies.

It is known from literature that nickel based catalyst with smaller active metal particle size and high degree of dispersion exhibits higher catalytic activity [62]. Since nano-particle catalysts have higher number of active sites per gram, these catalysts should have better performance than micro-particle catalysts on the mass basis in gasification as stated by Li et al. However, more study is also needed to validate if there is any size effect per unit active site of the catalyst.

5. Future directions of biomass gasification

Conventional biomass gasification is commonly performed by using one of the following reactor setups:

- fluidized bed gasifier with downstream catalytic tar cleaning reactor;
- fast pyrolysis reactor with downstream catalytic steam reformer;
- catalytic fluidized bed gasifiers.

Fluidised bed reactors are capital intensive and hence large scale reactors are required to make it economical. According to a study conducted by Leung et al., cost of the gasifier and gas cleaning system can account for 66.7–85.5% of the total capital cost [54]. This is particularly true for fluidized bed gasifier due to the high cost of blower, continuous feed systems and control systems. In comparison, capital cost of fixed bed reactors for biomass gasification is significantly lower. Therefore, a novel approach called as reactive flash volatilisation, was recently proposed for cellulose gasification [44]. Reactive flash volatilisation uses a fixed bed gasifier with carbon space velocity and carbon mass flow rate significantly higher than fluidised bed reactors.

Reactive flash volatilization, which combines pyrolysis and partial oxidation, was first introduced by Salge et al. for synthesis gas production from non-volatile fuels such as refined soy oil, biodiesel and aqueous sugar solution [73]. As illustrated in Fig. 4, one of the biggest advantages of this reactor is lower amount of catalyst used per unit mass of carbon feedstock compared to the fluidised bed gasifiers. According to Colby et al. [44], conventional biomass gasification setup-up, such as fluidized bed gasifier with downstream catalytic tar cleaning reactor or catalytic fluidized bed gasifier, has carbon mass velocity of 0.8–9.0 h^{−1}. In comparison, reactive flash volatilization has carbon mass velocity of 50.0–80.0 h^{−1}. Although similar carbon mass velocity can be achieved with fast pyrolysis reactor with downstream catalytic steam reformer, size of the reactive flash volatilization reactor is at least an order of magnitude smaller than other reactors (Fig. 4). Carbon space velocity of 100–300 mol L^{−1} h^{−1} can be easily attained with reactive flash volatilization. Because of its high carbon space

velocity (mol C/L_{reactor} h) and high carbon mass flow rate (g C/g_{cat} h), reactive flash volatilization reactors can be economical at a small scale, which is important for decentralized biomass gasification [74]. Small scale gasification plants can be placed closer to the feedstock source which minimizes transportation cost of low energy density biomass.

In Salge et al.'s study, synthesis gas was produced with Rh–Ce catalyst where non-volatile feed are decomposed into hydrogen and carbon monoxide in less than 50 ms without the production of carbon [73]. The formation of carbon was avoided by rapidly oxidizing the decomposition products into gases. The heat generated from oxidation reaction prevented condensation reactions that might lead to rapid carbon formation. 99% conversion of the feed at ~70% hydrogen selectivity was achieved without catalyst deactivation of at the end of 20 h run. Lower C/O ratio led to higher catalyst bed temperature, feed conversion, and hydrogen and carbon monoxide selectivities.

Cellulose gasification using reactive flash volatilization was conducted by Colby et al. [44]. This is a more complex process compared to the liquid feeds because it involves pyrolysis, partial oxidation, steam reforming, and water–gas shift reactions. 2 wt% Rh–2 wt% Ce/Al₂O₃ catalyst was used for microcrystalline cellulose gasification which produced C₁ products within 24–33 ms residence time temperature of 600–825 °C. Increasing the C/O ratio increased the hydrogen and CO yield. Whereas, increasing the S/C (steam to carbon) ratio increased the hydrogen yield and decreased the CO yield, which is attributed to forward water–gas shift reaction. Selectivity of hydrogen was 14–47% and selectivity of carbon monoxide was 21–38%.

Reactive flash volatilization with Rh based catalyst is a promising method for high quality syngas production but it is impractical for larger than bench scale application due to the high cost of the Rh–Ce catalyst. Moreover, lignocellulose feedstock must be used instead of purified microcrystalline cellulose to make this process commercially viable. Gasification of lignocellulose feedstock will be a greater challenge for the catalysts. Therefore, it is necessary to develop a cost effective and robust catalyst for reactive flash volatilization of lignocellulose. Further research is required to study the effectiveness of this process in raw biomass gasification. In this regard, nickel catalysts discussed in this paper (supported, unsupported, promoted, nanoparticles etc.) may play a vital role.

6. Conclusion

Nickel catalyst has been widely employed in various chemical processes for decades. It has been proven as one of the most cost effective transition metal catalyst, especially in eliminating tar and improving the quality of the product gas of biomass gasification. However, various reports have pointed out that these catalysts suffer rapid deactivation as a primary catalyst in the gasification due to carbon fouling, sintering and morphological changes. Nonetheless, nickel based catalyst is still very effective in tar steam reforming and adjusting the CO–H₂ ratio when used as secondary catalyst in a downstream reactor.

Key factors that define the catalytic activity of the nickel based catalyst are the metal particle size and its dispersion. Small crystallite size and high degree of dispersion of nickel on the supports lead to high catalytic activity. Catalytic activity can also be improved by the addition of metal promoter, such as Pt, Co and Cu. These metal promoters improve the reaction activity through enhancing the nickel metal reducibility by forming strong interaction with nickel metal. Metal promoters also enhance dispersion of the nickel metal on the support and provide higher resistance to coke formation.

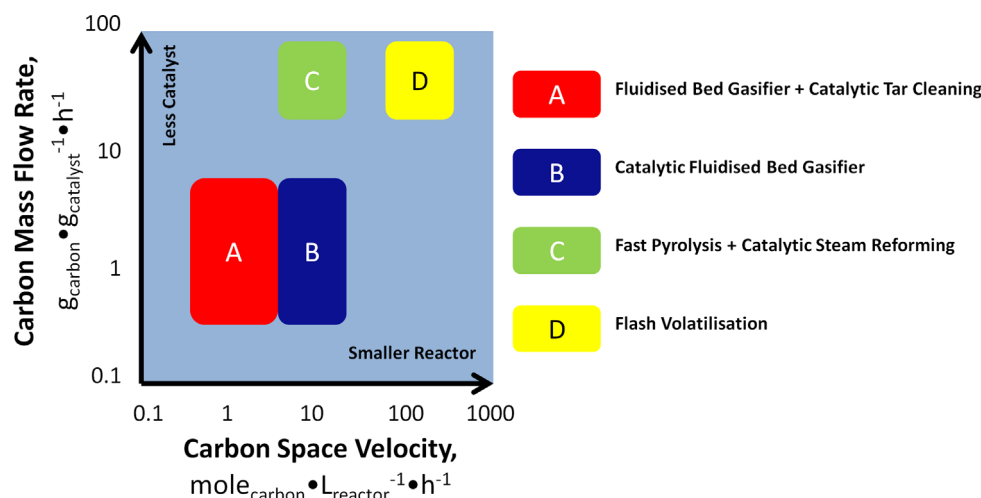


Fig. 4. Comparison of the space velocity, mass flow rate, amount of catalyst required and reactor size of various reactor setups.
Source: (Adapted from [44]).

Coke deposition on catalyst, which results in deactivation, is the primary concern in catalytic biomass gasification and pyrolysis. The amount of coke deposition is associated with the types of supports used. Basic supports are more coke resistant than acidic supports. Carbon deposition can be reduced by addition of alkaline earth metals and effective use of catalyst supports such as dolomite and MgO.

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